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(54) Title: ELASTOMERIC ARTICLES			
(57) Abstract			
<p>There is described a method of manufacturing elastomeric thin walled articles, and thin walled elastomeric articles manufactured therefrom, which comprises dipping a suitably shaped former into an aqueous polyurethane emulsion having a plasticizer of half ester of dicarboxylic acid which does not form an acid anhydride readily, an alkoxy-substituted aliphatic monohydric alcohol and salts of the half ester.</p>			

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ELASTOMERIC ARTICLES

This invention relates to elastomeric thin walled articles and methods for their preparation.

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Elastomeric thin walled articles, such as gloves for surgical use are generally manufactured from natural rubber, usually by dipping a glove former into a vessel containing natural rubber latex. However, recently problems have been encountered with natural rubber surgical gloves since small quantities of proteins may leach from the glove into an open surgical site and in some instances cause an allergenic reaction to the patient.

Attempts have been made to manufacture surgical gloves from synthetic materials such as polyurethane. US Patent No.4463156, McGary et al, describes in Example 14, the manufacture of a mixed diol, 4,4'-diphenylmethane diisocyanate polyurethane. A 20% solids solution of the polyurethane was prepared and a glove produced by dipping a glove former into the suspension. McGary discloses that the polyurethane gloves have a tensile strength of from 24.1 to 44.8 MPa. Also, polyurethane suspensions suffer from the disadvantage that they tend to be fairly unstable on storage and therefore do not lend themselves to production processes.

European Patent application No.0413467 discloses polyurethane condoms which are manufactured by dipping a suitably shaped former into an organic solvent solution of a polyurethane. However, such processes have a major disadvantage in that undesirable solvents must be used thus giving rise to increased costs and problems with waste products.

Sadowski et al (J S Sadowski, B Martin and D D Gerst, "Polyurethane Latexes for Coagulation Dipping", Elastomerics, August 1978, 17-20) describes that polyurethane gloves may be made by the "Anode" process, that is, by dipping a former into a coagulant bath, followed by dipping into a polyurethane latex. The polyurethane in the latex was of a particle size in the range of from 60 to 300nm. The latex also comprised a non-ionic surfactant. However, although in 1978

Sadowski alleged that suitable gloves may be formed, to date, polyurethane gloves manufactured by coagulation dipping have never been made commercially available. Thus there has been a long felt want for a commercially viable process for the emulsion dipping of polyurethane articles and polyurethane gloves in particular.

We have now surprisingly found that certain polyurethanes with a larger particle size than that disclosed by Sadowski can advantageously be formed into aqueous emulsions which are sufficiently unstable to electrolytes to permit thin layer coatings to be formed, eg. in the manufacture of gloves, and whilst the emulsions possess adequate shelf life. Furthermore, we have found that articles made from such polyurethane emulsions have tensile strength values not disclosed by McGary.

Thus according to the invention we provide a thin walled polyurethane article having a tensile strength of up to 24 MPa.

We prefer thin walled polyurethane articles having a tensile strength of from 10 to 24 MPa.

The improved tensile set properties may be obtained by including a plasticiser in the polyurethane emulsion. In particular we have found that specific plasticisers are advantageous. Particularly preferred plasticisers are those disclosed in Canadian Patent No.959857.

Thus according to the invention we further provide a thin walled polyurethane article wherein the polyurethane comprises a plasticiser which plasticiser comprises a half-ester of a dicarboxylic acid which does not form an acid anhydride readily and an alkoxy-substituted aliphatic monohydric alcohol having between 3 and 20 carbon atoms, and salts of said half-ester, said dicarboxylic acid having the following structure;



wherein R is $-(\text{CH}_2)_n-$ or $-\text{CH}=\text{CH}-\text{CH}_2-$,

and $n = 0, 1$ and 4 to 6 carbon atoms.

According to a further feature of the invention we provide a thin walled polyurethane article wherein the polyurethane comprises from 0.1 to 40% w/w of a plasticiser as hereinbefore described, preferably from 0.1 to 20% w/w.

Thus according to the invention we also provide a method of manufacturing a thin walled polyurethane article which comprises dipping a shaped former into an aqueous polyurethane emulsion comprising a plasticiser as hereinbefore described.

The amount of plasticiser present in the polyurethane emulsion may be from 0.1 to 40% w/w, preferably from 0.1 to 20% w/w and especially from 0.1 to 10% w/w, eg. 5% w/w plasticiser. Plasticisers which may be mentioned include diethylene glycol monobutyl ether hydrogen adipate, ethylene glycol monohexyl ether hydrogen fumarate, butynediol monomethyl ether hydrogen adipate, butynediol monobutyl ether hydrogen adipate, diethylene glycol monoethyl ether hydrogen malate, 2-methoxyethyl hydrogen suberate, 2-butoxyethyl hydrogen isophthalate, 2-butoxyethyl hydrogen terephthalate, p-methoxybenzyl hydrogen fumarate, 3-ethoxy-1-propyl hydrogen pimelate, 2-propoxyethyl hydrogen adipate, 2-butoxyethyl hydrogen oxalate, ethylene glycol monobutyl ether hydrogen adipate and metal salts thereof.

The plasticisers described herein may be manufactured using processes described in Canadian Patent No.959857.

We also provide a method of manufacturing a thin walled polyurethane article which comprises dipping a shaped former into an aqueous polyurethane emulsion as hereinbefore described which emulsion comprises a substantial number of particles with a mean particle size of greater than 0.3 μ m and a plasticiser.

By the term mean particle size is meant the mean diameter for generally spherical particles. The mean particle size of polyurethane emulsions can be measured using conventional methods known *per se*, such as electron microscopy or a conventional particle size analyser, eg. a Malvern Analyser. The mean particle size may be from 0.31 μ m to 2.5 μ m,

preferably from 0.5 μ m to 2.0 μ m, more preferably from 0.5 μ m to 1.5 μ m, eg. 1.0 μ m.

Thus a substantial number of the particles in the polyurethane emulsion may have a particle size of greater than 0.3 μ m. By the term substantial number, we mean at least 50% w/w, preferably at least 70% w/w and more preferably at least 80% w/w and especially at least 90% w/w of the particles have a particle size of greater than 0.3 μ m when measured using electron microscopy. Similarly a substantial number of particles fall within the limits of the preferred mean particle sizes hereinbefore defined.

In particular we have found the presence of surfactant in the polyurethane emulsion as hereinbefore described increases the stability of a large particle size polyurethane emulsion and provides advantageous film forming properties. Thus, in the manufacture of thin walled articles it may be advantageous to have a surfactant present.

Thus according to the invention we provide a method as hereinbefore described wherein the polyurethane emulsion as hereinbefore described comprises from 0.1 to 10% w/w of surfactant, preferably from 2 to 8% w/w and especially from 4 to 6% w/w, eg. 5% w/w.

The amount of surfactant may vary according to the type of surfactant used, the nature of the polyurethane, the particle size of the polyurethane, the solids content of the emulsion, etc. Generally however, the amount of surfactant present should be at least sufficient to exceed the critical micelle concentration in the emulsion. More particularly, it is preferred to use an amount of surfactant in the emulsion so that the surface tension of the emulsion, measured using conventional methods known per se, approaches that of natural rubber latex. Thus, it is preferred that the emulsion possesses a surface tension of from 20 to 50 dynes cm⁻¹, preferably from 25 to 45 dynes cm⁻¹, more preferably from 30 to 40 dynes cm⁻¹, eg. 35 dynes cm⁻¹.

Any conventional surfactant may be used including non-ionic surfactants, ionic surfactants, eg. anionic surfactants, or a mixture of two or more ionic and non-ionic surfactants. Of the ionic surfactants, anionic

surfactants are preferred. Examples of suitable anionic surfactants include carboxylate surfactants. Carboxylate surfactants are typically derived from C10 to C20 straight chain fatty acids which may optionally be saturated or unsaturated. Conventionally known salts of carboxylate surfactants may be used, such salts include ammonium or alkyl ammonium salts, eg. triethylamine or morpholine salts; or alkali metal salts, eg. sodium or potassium salts. In addition to the fatty acids, salts of other acids may be used including oleic, ricinoleic and rosin acids or the n-alkyl sarcosides. The invention is not limited to the surfactants hereinbefore described and may also include mixtures of two or more surfactants.

Non-ionic surfactants are particularly preferred and examples of suitable non-ionic surfactants include those described in "Surfactant and Interfacial Phenomens" Milton J Rosen, (John Wiley & Sons Inc (1978)). Examples of non-ionic surfactants which may be mentioned are, polyoxyethylene alkylphenols; alkylphenol ethoxylates, examples of alkylphenols are p-nonylphenol, p-octylphenol or p-dodecylphenol; polyoxyethylenated straight chain alcohols; alcohol ethoxylates (the alcohols are typically derived from coconut or tallow oils or are synthetic long carbon chain alcohols); polyoxyethylenated polyoxypropylene glycols (derived from ethylene oxide and propylene oxide); polyoxyethylenated mercaptans; long chain carboxylic acid esters, eg. glycerol and polyglyceryl esters of natural fatty acids, propylene glycol, sorbitol and polyoxyethylenated sorbitol esters; polyoxyethylene glycol esters and polyoxyethylenated fatty acids; alkanolamine condensates; alkanolamides, eg. alkanolamine/fatty acid condensates; and tertiary acetylenic glycols.

We have found that the use of surfactant in the polyurethane results in residual surfactant being present in the thin walled article. Thus according to the invention we provide a thin walled polyurethane article comprising from 0.1 to 40% w/w of a plasticiser as hereinbefore described and from 0.1 to 10% w/w of surfactant. Preferably the thin walled article comprises from 2 to 10% w/w surfactant more preferably from 4 to 10% w/w and most preferably from 6 to 8% w/w.

The concentration of the polyurethane in the aqueous emulsion, ie. the solids content, may be from 10 to 60% w/w, preferably 20 to 60% w/w, preferably 40 to 60% w/w, and especially 45 to 55% w/w, eg. 52 to 53% w/w.

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The molecular weight of the polyurethane in the emulsion may vary, but preferably the weight average molecular weight (M_w) is from 50,000 to 1,000,000, more preferably from 50,000 to 800,000. The number average molecular weight (M_n) may be from 4000 to 1500, preferably from 5000 to 12000. Emulsions are especially preferred wherein the molecular weight distribution tends to be binodal, that is, the emulsion comprises a relatively high molecular weight component and a relatively low molecular weight component. Thus the relatively high molecular weight component may have a weight average molecular weight in the region of from 50,000 to 150,000, preferably from 75,000 to 125,000, eg. 100,000, whilst the relatively low molecular weight component may have a weight average in the region of from 1000 to 2000, preferably from 1200 to 1800, eg. 1600. The relative ratio of the high molecular component to the low molecular weight component may be from 4:1 to 3:2, preferably 3:1.

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According to the invention we also provide a thin walled polyurethane article comprising from 0.1 to 40% w/w of a plasticiser as hereinbefore described wherein the polyurethane has a weight average molecular weight of from 50,000 to 1,000,000.

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In addition the polyurethane emulsion may comprise a salt forming moiety to confer dispersibility, such as an amine, eg. diethanolamine or morpholine, or a cationic species, eg. sodium, potassium, ammonium, etc. Preferred amines include tertiary amines and especially tertiary alkyl amines, such as triethylamine.

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We further provide the use of an aqueous polyurethane emulsion comprising a plasticiser as hereinbefore described in the manufacture of a thin walled polyurethane article according to the invention.

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A variety of polyurethanes may be used in the manufacture of the articles of the invention. However, preferred polyurethanes are anionic polyurethanes and especially those prepared from polyethers or

polyesters. Aromatic polyesters may be used but aliphatic polyesters are preferred. Similarly, although aromatic diisocyanates may be used, aliphatic diisocyanates are preferred. It is especially preferred to use diisocyanates which can render flexibility to the polyurethane, such as cyclohexane diisocyanates and alkylcyclohexane diisocyanates. Preferred polyurethanes are those sold under the name UCECOAT (Trade Mark), such as UCECOAT XE102. The most preferred polyurethanes are those sold under the name WITCOBOND (Trade Mark) available from Baxenden in the UK. WITCOBOND 740 is especially preferred.

Thus according to the invention we provide a thin walled article made from a plasticiser as hereinbefore described and a polyurethane selected from WITCOBOND and UCECOAT, especially WITCOBOND, eg. WITCOBOND 740.

The method according to the invention may advantageously include a coagulant dipping step in the process. Thus according to the invention we provide a method of manufacturing a thin walled polyurethane article which comprises first dipping a suitably shaped former into a coagulant solution, optionally drying the coagulant coated former, followed by dipping the coagulant coated former into a polyurethane emulsion comprising a plasticiser as hereinbefore described.

Preferred coagulants are ionic coagulants, eg. mono, di- and tri-valent cations. Examples of monovalent cationic coagulants include quaternary ammonium salts such as cyclohexylamine salts, eg. cyclohexylamine acetate. Divalent cationic coagulants are preferred, such as alkaline earth metal salts, eg. calcium salts, or transition metal salts, eg. zinc salts. The nitrates of these salts are preferred and thus the most preferred coagulant is calcium nitrate. In addition to conventional coagulants, heat sensitising agents may also be used. Thus heat sensitising agents such as polyether siloxanes may be used, such agents are sold as coagulant WS by Bayer. Heat sensitivity coagulants are generally mixed with the polyurethane emulsion. The amount of coagulant present in the coagulant solution may be from 5 to 60% w/w solution, preferably from 5 to 30% w/w, preferably from 5 to 20% w/w, more preferably 8 to 12% w/w and especially 10% w/w.

The method according to the invention may also include a curing step. Thus following dipping an appropriately shaped former into a polyurethane emulsion the formed article may be cured at from 60° to 150°C, preferably from 60° to 120°C and more preferably from 70° to 100°C, eg. 90°C. Curing times may vary according to, inter alia, the thickness of the formed article. Curing times of from 5 to 60 minutes are appropriate.

10 In addition, the method according to the invention may include a leaching step. Leaching may be carried out before or after curing the formed article, or leaching may be carried out both before and after curing.

15 The leaching process is intended to, inter alia, remove residual coagulant and/or surfactant. It may be a characteristic of the thin walled polyurethane articles according to the invention that residual coagulant and/or surfactant may remain in the polyurethane.

20 Thus according to a further feature of the invention we provide a thin walled polyurethane article wherein the polyurethane comprises a plasticiser as hereinbefore described and a coagulant residue of from 2 to 15mg/g (of polyurethane) preferably from 2 to 12mg/g, more preferably from 3 to 10mg/g.

25 In the case of calcium nitrate coagulant the residual coagulant may be detectable in the form of calcium ions. Thus conventional techniques known per se may be used in, eg. calcium ion analysis. Such methods include, inter alia, atomic absorption spectrometry.

30 Additives may be included in the coagulant solution or the emulsion to improve the release properties of the polyurethane article allowing the cured article to be more easily removed from the former. The stripping of the article from the former may be improved by the inclusion of a detackifier. Any conventional detackifiers may be used including powders
35 such as chalk, starch, eg. maize starch or corn starch, slays, lycopodium powders, talc or ground whiting. In addition liquid detackifiers conventionally used with natural rubbers may be used, these include silicone emulsions, silicone oils or polypropylene glycols.

The thin walled articles manufactured by the process of the invention may also be detackified by surface treatment, such as chlorination or bromination or surface coating. The powdered detackifiers may be applied in the coagulant or after the glove has been cured, but the preferred detackifiers are carbonates, such as alkaline earth metal carbonates, eg. calcium carbonate. The level of detackifier present in the glove may vary, but preferred levels are from 0.1 to 10% w/w, preferably from 2.5 to 7.5% w/w, most preferably 5% w/w.

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The thickness of the flexible thin walled polyurethane articles may be from 0.03 to 1.0mm, preferably from 0.05 to 0.8mm and especially from 0.05 to 0.5mm.

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Such articles are advantageous in that the tensile strength or the force required to break the polyurethane remains sufficient to give the article utility. Thus we further provide a flexible thin walled polyurethane article having a tensile strength of from 2 MPa to 60 MPa. Such tensile strength is preferably from 5 to 40 MPa, more preferably from 10 to 40 MPa and especially from 15 to 40 MPa, eg. 24 to 40 MPa.

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In addition, the articles according to the invention have an advantageous value for elongation at break. According to the invention we provide a flexible article made from polyurethane having an elongation at break of greater than 450%, eg. 500 to 600%, eg. 550%.

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The thin walled articles of the invention include gloves, eg. gloves for surgical use, condoms, sleeves, catheters, boots, bladders, balloons, teats, enema tips and other tubular articles.

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The invention will now be illustrated but in no way limited by the following Examples in which temperatures are in degrees Celsius.

Example 1

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Tensile Test

A 4mm wide dumbbell cutter was used to cut a sample of film. Reflective markers stuck to the parallel part of the test piece identified a

25mm length. A tensile test was carried out with a crosshead speed of 500mm min⁻¹ using a Zwick 1435 tensile testing machine. An extensometer measured the true strains during the test by following the reflective markers. The stresses at 100, 300 and 500% strain were recorded along with the stress and strain at break.

Example 2

Tensile Set

Set is defined as the permanent deformation following the application and removal of strain. A 4mm wide dumbbell cutter was used to cut a sample of film, and reflective markers were stuck on about 25mm apart. The sample was stretched to 300%, and immediately relaxed. The second gauge length between the reflective markers was measured under a very small load. Percentage set is defined as:

$$\% \text{ set} = \frac{(2\text{nd gauge length} - 1\text{st gauge length}) * 100\%}{(1\text{st gauge length})}$$

Example 3

Molecular Weight Determination

Molecular weight of the polyurethane was analysed using EASICAL (Trade Mark) polystyrene standards dissolved in tetrahydrofuran (2ml, 0.2%) by allowing the standard mix stick to stand in tetrahydrofuran for 30 minutes. The polyurethane samples were prepared using 0.03g of polyurethane dissolved in tetrahydrofurans (10ml) SOP/AD/170/246/262.

The samples were analysed using gel permeation chromatography (GPC) and a refractive index detector.

Example 4

Coagulant Content

The calcium content of polyurethane films was determined after ashing the samples of the polyurethane film, taking up the ash in water (25ml) and then diluting further as appropriate. Calcium standards at 1.0, 2.0, 3.0 and 4.0 µg/ml in water were used to quantify the calcium present.

Example 5**Surfactant Content**

- 5 The method used to determine the amounts of surfactant (nonyl phenol ethoxylate) present in batches of WITCOBOND 740 emulsion involved soxhlet extraction with methanol of the films produced after drying. Followed by HPLC analysis on the extracts produced.
- 10 Preparation of polyurethane film by evaporating to dryness the emulsion at 105° followed by soxhlet extraction of 0.7-0.8g portions of the film with methanol (ca.100ml) for 4 hours. Extracts were quantitatively transferred into 100ml volumetric flasks and subsequently analysed by HPLC alongside nonyl phenol ethoxylate (surfactant) standards.

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Example 6**Particle Size Determination****a) Malvern Analyser**

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- 25 The malvern particle size analyser is a light scattering based particle size analyser. It uses a 2 milliwatt Helium/Neon laser and a Fourier transform lens system to focus the scattered laser light on to a photosensitive silicon detector. The lens used was a 45mm lens which is used to measure particle diameters in the range of 0.1 to 80µm. The sample diluent was deionised water that had been filtered through a 0.2µm filter. The diluent particle size is measured prior to sample addition and is accounted for in the results as the background reading. The sample dilution was one drop from the end of a microspatula per 500ml of
- 30 diluent.

CLAIMS

1. A method of manufacturing a thin walled polyurethane article which comprises dipping a shaped former into an aqueous polyurethane emulsion which emulsion comprises a plasticizer having a half ester of dicarboxylic acid which does not form an acid anhydride readily, an alkoxy substituted aliphatic monohydric alcohol and salts of the half ester.
2. A method according to claim 1 wherein the emulsion comprises a substantial number of particles with a mean particle size greater than $0.3\mu\text{m}$.
3. A method according to claim 1 wherein the emulsion comprises a substantial number of particles with a mean particle size of from $0.31\mu\text{m}$ to $2.5\mu\text{m}$.
4. A method according to claim 1 wherein at least 50% of the particles have a mean particle size of greater than $0.3\mu\text{m}$.
5. A method according to claim 1 wherein the polyurethane emulsion contains from 0.1 to 10% w/w of a surfactant.
6. A method according to claim 8 wherein the surfactant is non-ionic.
7. A method according to claim 1 wherein the concentration of the polyurethane in the aqueous emulsion is from 10 to 60% w/w.
8. A method according to claim 1 wherein the polyurethane emulsion contains at least 5% w/w of a plasticiser.
9. A method according to claim 1 wherein the polyurethane has a weight average molecular weight of from 50,000 to 1,000,000.
10. A method according to claim 1 which comprises an additional step of first dipping the former into a coagulant solution and optionally drying the coagulant coated former.

11. A method according to claim 1 wherein the polyurethane comprise an aliphatic diisocyanate and an aliphatic polyester.

12. A method according to claim 11 wherein the polyurethane is
5 WITCOBOND.

13. A thin walled polyurethane article comprising from 0.1 to 10% w/w of a surfactant in the polyurethane.

10 14. A thin walled polyurethane article wherein the polyurethane comprises from 2 to 15mg/g (of polyurethane) of a coagulant residue.

15 15. A thin walled polyurethane article wherein the polyurethane comprises from 0.1 to 40% w/w of a plasticiser.

16. A thin walled polyurethane article wherein the polyurethane has a weight average molecular weight of from 50,000 to 1,000,000.

20 17. A thin walled polyurethane article wherein the polyurethane is WITCOBOND.

18. A thin walled article according to any one of the preceding claims wherein the article is a glove.

25 19. A thin walled article according to any one of the preceding claims wherein the article is a condom.

30 20. The use of an aqueous polyurethane emulsion containing a substantial number of particles with a mean particle size of greater than 0.3µm in the manufacture of a thin walled polyurethane article.

21. A method according to claim 1 wherein the dicarboxylic acid has the following structure:

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$$\text{HOOC(R)COOH}$$

Wherein R is $-(\text{CH}_2)_n$ and $n=0, 1, 4, 5$ or 6 .

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22. A method according to claim 1 wherein the dicarboxylic acid has the following structure:



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wherein R is $-\text{CH}=\text{CH}=\text{CH}_2-$.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/11763

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B28B 1/38; A41D 19/00; A61F 6/04

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS (AUTOMATED PATENT SYSTEM)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,779,975 (CLARK ET AL) 18 DECEMBER 1973, ENTIRE DOCUMENT.	1-22
Y	US, A, 3,981,945 (ATTWOOD ET AL) 21 SEPTEMBER 1976, ENTIRE DOCUMENT.	1-22
Y	US, A, 3,984,604 (KING ET AL) 05 OCTOBER 1976, ENTIRE DOCUMENT.	1-22
Y	US, A, 4,020,046 (KING ET AL) 26 APRIL 1977, ENTIRE DOCUMENT.	1-22
Y	US, A, 4,090,993 (ATTWOOD ET AL) 23 MAY 1978, ENTIRE DOCUMENT.	1-22
Y	US, A, 4,425,161 (SHIBAHASHI ET AL) 10 JANUARY 1984, ENTIRE DOCUMENT.	1-22

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US95/11763**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

264/304, 305, 306;
2/161.7, 161.8, 167, 168;
128/842, 844, 918

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

264/304, 305, 306;
2/161.7, 161.8, 167, 168;
128/842, 844, 918